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Chlorine Atom Reaction Kinetics Under Lower Stratospheric and Upper Tropospheric Conditions

Abstract

The reaction kinetics of many critical atmospheric reactions remain poorly understood under relevant atmospheric temperatures and pressures. Of particular importance are reactions involving chlorine atoms, which play a crucial role in many catalytic loss cycles. The uncertainty in this data limits the accuracy of models to forecast the trends of key atmospheric species. This work plans to study key chlorine atom reaction kinetics, including:

$$Cl + CH_4 \rightarrow CH_3 + HCl \qquad (1)$$
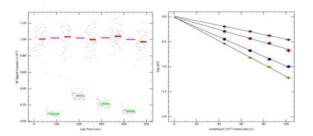$$ClOO + NO + M \rightarrow O_2 + ClNO + M \qquad (2)$$

Both of these reactions represent a sink for Cl atoms. Reaction 1 has been studied extensively, but not at low T. Reaction 2 has only recently been identified as a potential loss process, and requires further study at low temperature due to its thermal instability.

Experimental

* 5" diameter makes the system essentially wall-less.
* Four separate resonance fluorescence (RF) axes detect Cl atoms in the reaction zone.
* Cl atoms are produced via microwave discharge.
* Low temperatures are achieved by the simultaneous cryogenic cooling of the walls and the carrier gas.
* Excess reagent is injected upstream via loop injector to ensure complete mixing.
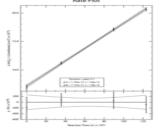
Results

Figure 3. The decays from figure 2 are plotted versus their corresponding axis, yielding the rate constant. Since the velocity of the flow is known, the inter-axis spacing can be converted to time. Reaction time is defined as 0 at the first axis: the x-intercept indicates where the radical and reagent first mix. The lower panel shows the fit residuals with a 95% confidence interval.

Future Experimental Work

*System is primed for cold temperature data.

*Modify RF axis to increase signal: this is of particular importance when introducing oxygen to the system due to it's absorption in the same region as Cl.

Impact

•Chlorine Kinetics
* This work will elucidate key reactions in the upper atmosphere and improve the accuracy of models that are used to predict future global trends in ozone loss and other key public health issues.

•Future Possibilities
* Only a few minor modifications are needed to allow the system to measure other key radicals: the work here paves the way for a vast array of future studies involving a large variety of crucial atmospheric species.

Acknowledgments

References

1. Sander, S. P et al. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*; Jet Propulsion Laboratory Publication No. 02-25, 2003

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